Supporting Information

Department of Chemistry, The University of Western Ontario, London, Ontario, Canada N6A 5B7

corrigan@uwo.ca 1-519 661-2111 ext 86387

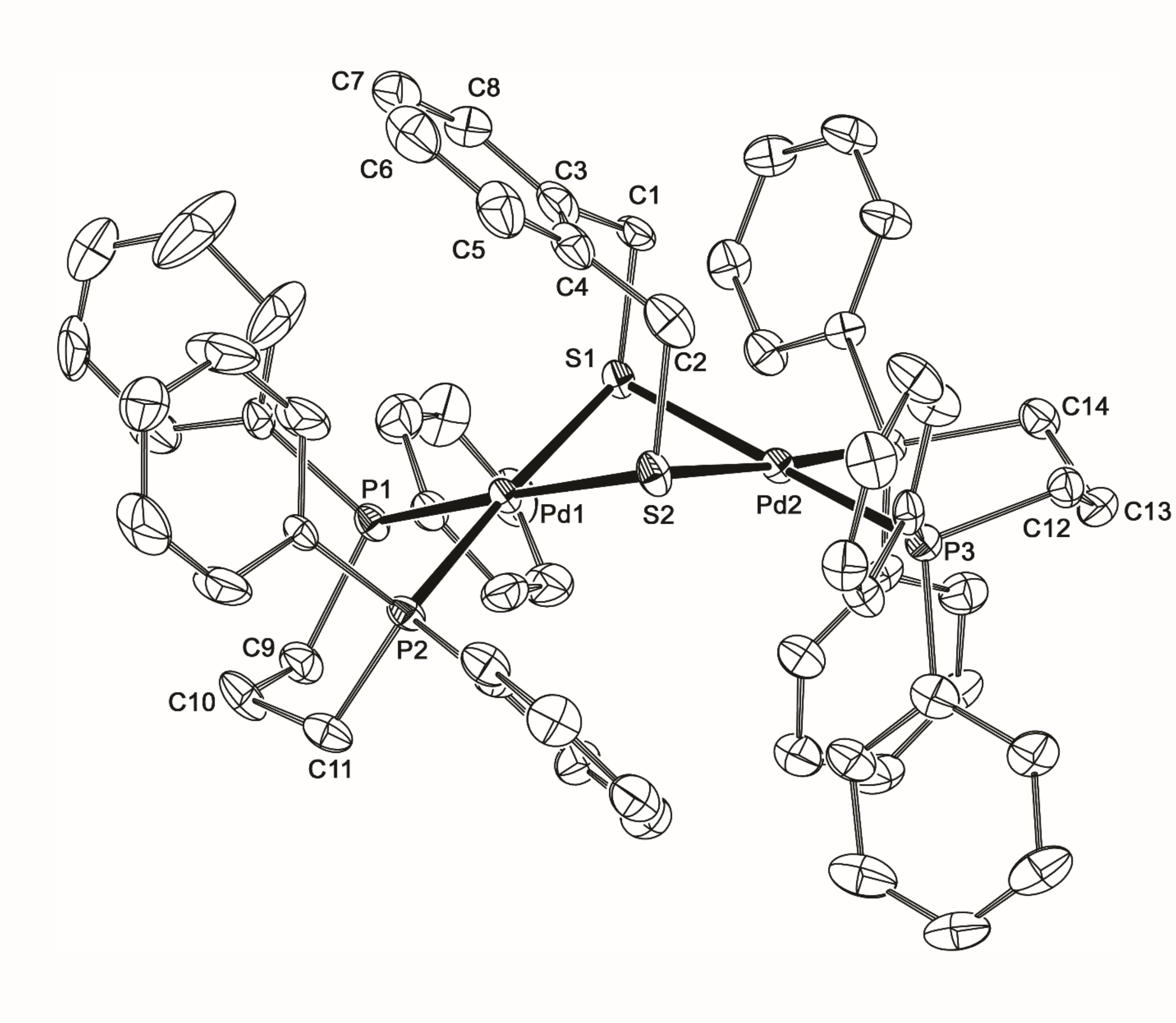

Fig. S1. The molecular structure of complex [**2a**]$^{2+}$. The thermal ellipsoids have been drawn at 40% probability. Hydrogen atoms, solvent molecules and counter ions have been omitted for clarity.

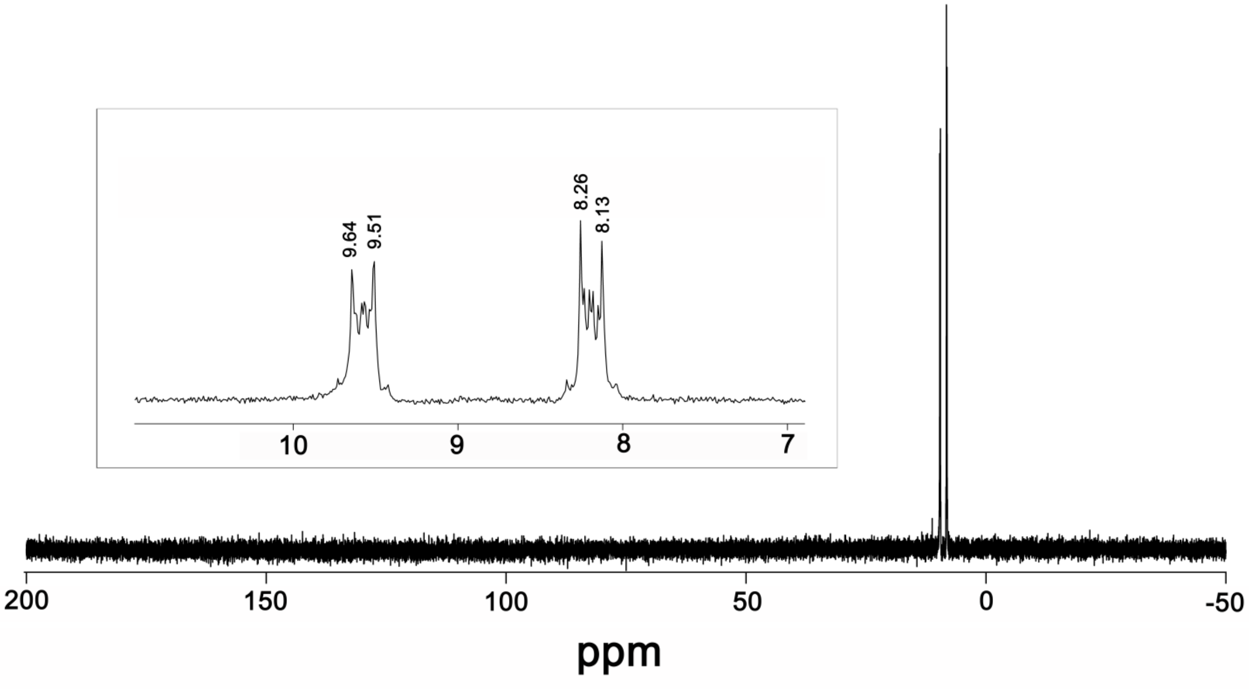

Fig. S2. $^{31}P\{^1H\}$ NMR spectrum of [**2a**]X_2 ($CDCl_3$, 25 °C, 161.97 MHz).

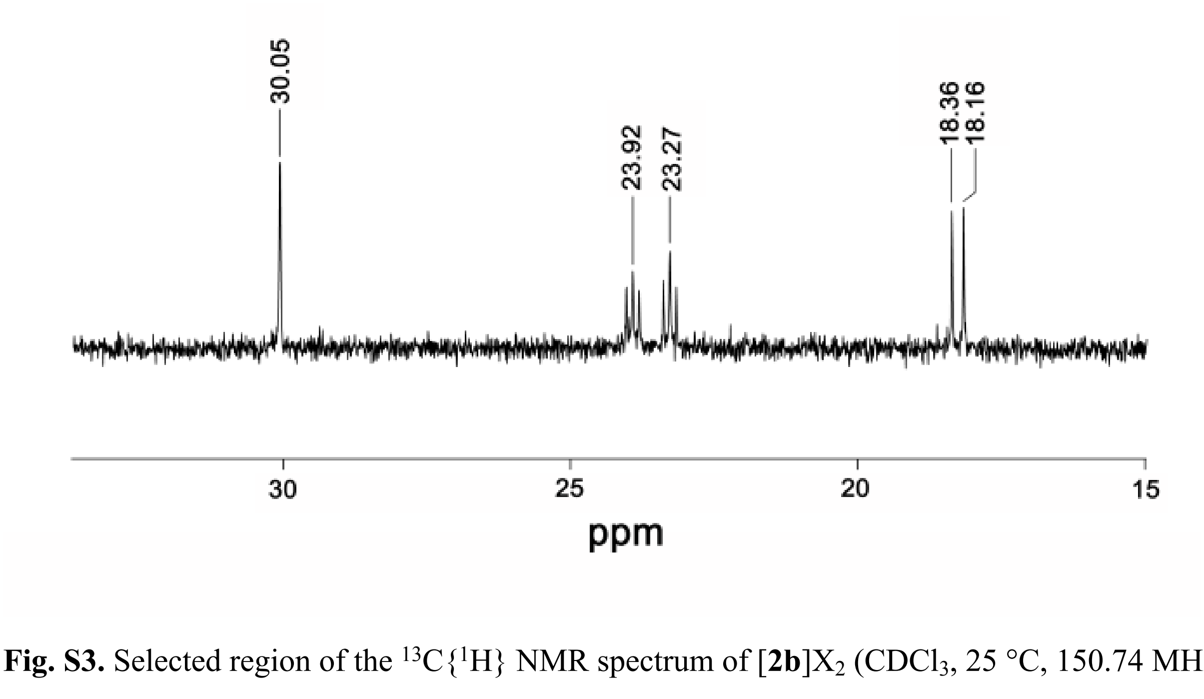

Fig. S3. Selected region of the $^{13}C\{^1H\}$ NMR spectrum of [**2b**]X_2 ($CDCl_3$, 25 °C, 150.74 MHz).

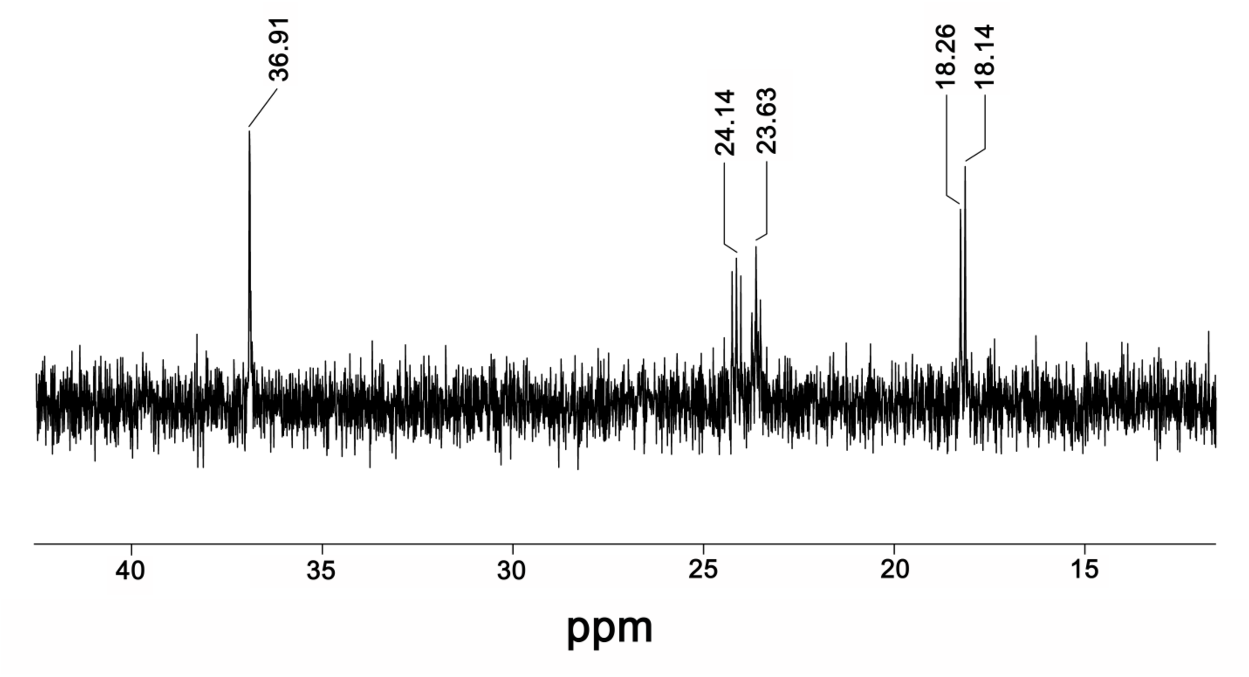

Fig. S4. Selected region of the $^{13}C\{^{1}H\}$ NMR spectrum of [**2a**]X_2 ($CDCl_3$, 25 °C, 150.74 MHz).

NMR discussion of the propyl groups on the diphenylphosphine propane (dppp) ligands

Two discrete sets of peak for each pair indicates that axial and equatorial protons of -CH_2- groups of dppp are magnetically different. The sets of peaks at 2.34 and 2.46 ppm in ^1H (for [**2b**]X_2) can be assigned as two overlapped doublets. The psudo-triplets at 4.04 and 4.67, likely arises from two overlapped doublets. It reveals the slightly difference between the axial and equatorial protons of the side –CH_2- groups on one chain. On the other hand, the sets of peaks at 1.11 and 1.42 ppm are assigned for the middle –CH_2- groups of the propane chains. The ^1H-^{13}C HSQC reveals that these sets accompanying with the peaks between 2.30-2.50 ppm are correlated with the two singlet resonance at 18.2 and 18.4 ppm in ^{13}C spectrum. Presumably, like their neighbouring methylene groups, each middle –CH_2- shows two sets of peaks for axial and equatorial protons as well, which one sets appears at higher field (1.11 and 1.42 ppm) and the other ones are buried under the other sets at 2.30 to 2.50 ppm (Figure 5b). The same pattern is observed at the ^1H-^{13}C HSQC of [**2a**]X_2 (Figure S5b). The expected doublet peaks between 2.3 to 2.6 ppm are shown in the expanded region of Figure 5b for [**2b**]X_2.

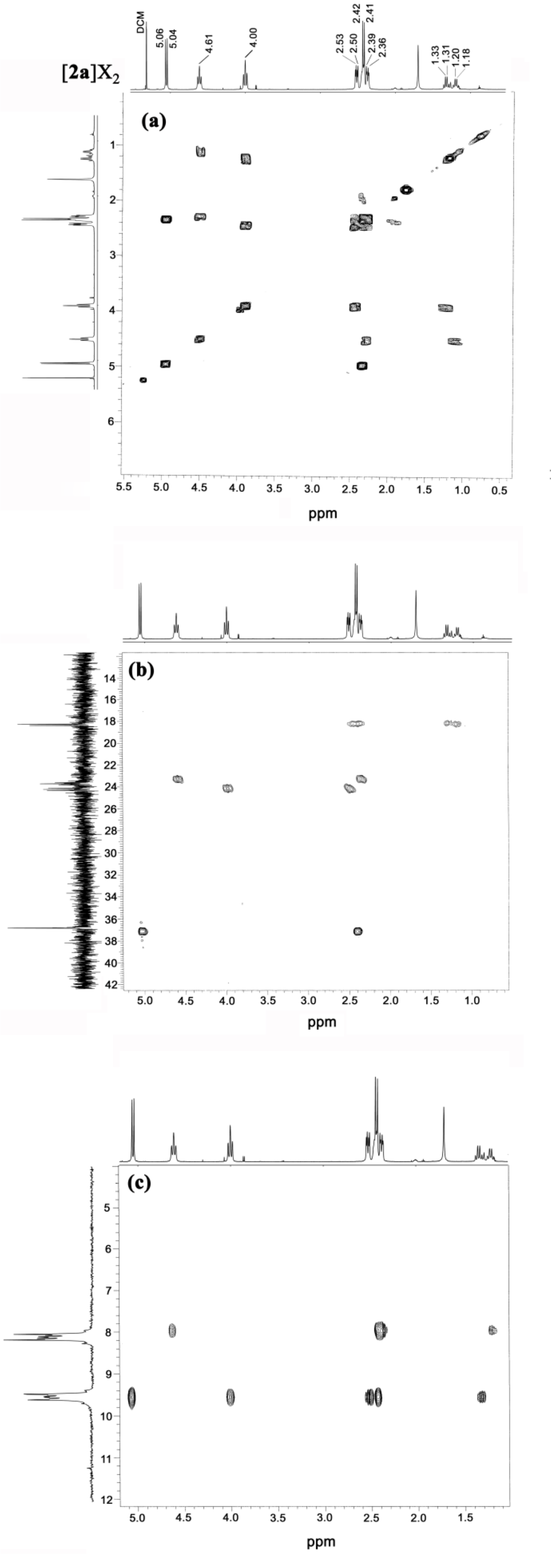

Fig. S5. Selected region of 2D NMR spectra of [**2a**]X_2; (a) ^{1}H–^{1}H COSY (CD_2Cl_2, 25 °C, ^{1}H; 400.08 MHz) (b) ^{1}H–^{13}C HSQC (CD_2Cl_2, 25 °C, ^{1}H; 399.76 MHz, ^{13}C; 100.52 MHz) (c) ^{1}H–^{31}P HMBC (CD_2Cl_2, 25 °C, ^{1}H; 599.47 MHz, J = 16 Hz).

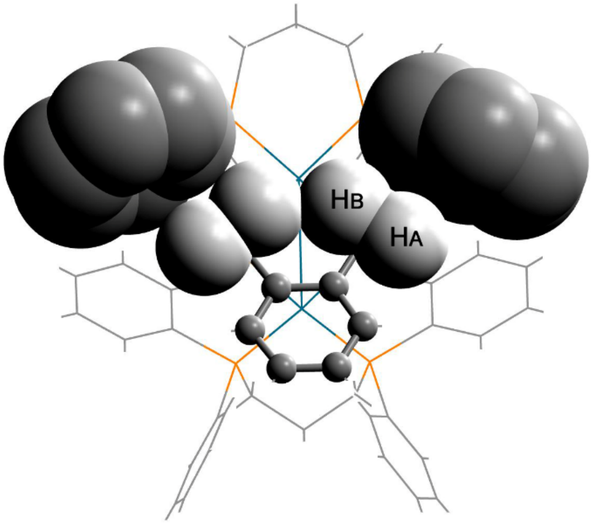

Fig. S6. A view of molecular structure of [**2b**]X_2 showing different environment around protons of the metylene groups on the bridging ligand. Other hydrogen atoms, solvent molecules and counter ions have been omitted for clarity.

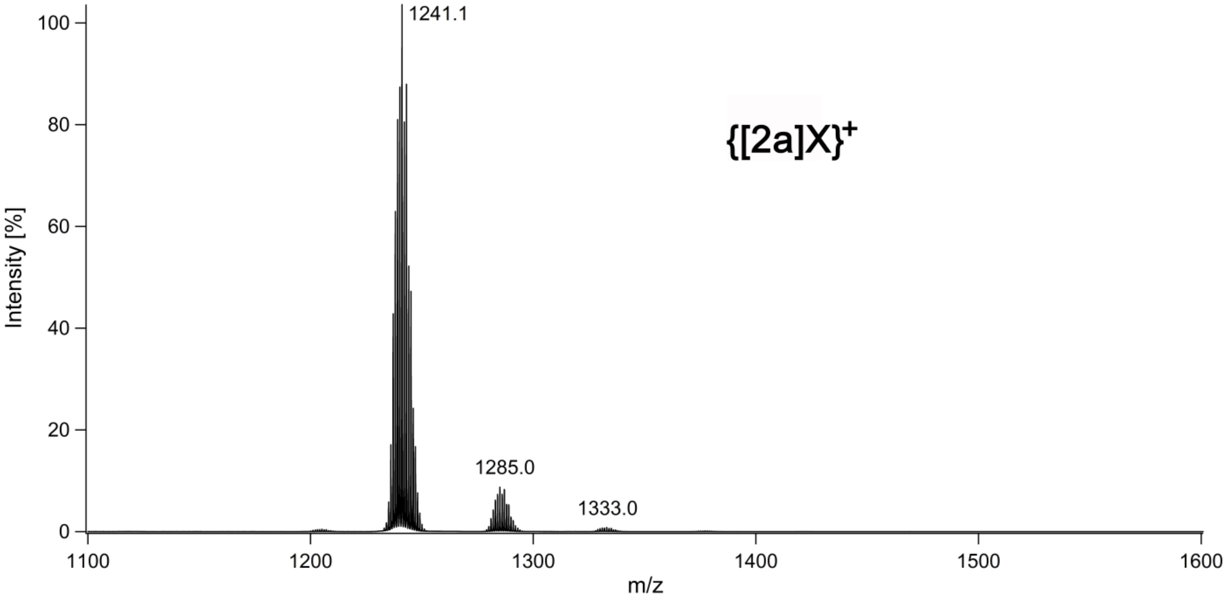

Fig. S7. Mass spectrum obtained by electrospraying [**2a**]X_2 in dichloromethane at an ESI capillary voltage of 4.5 kV. Charge states are indicated as 1+ for different counter ions.

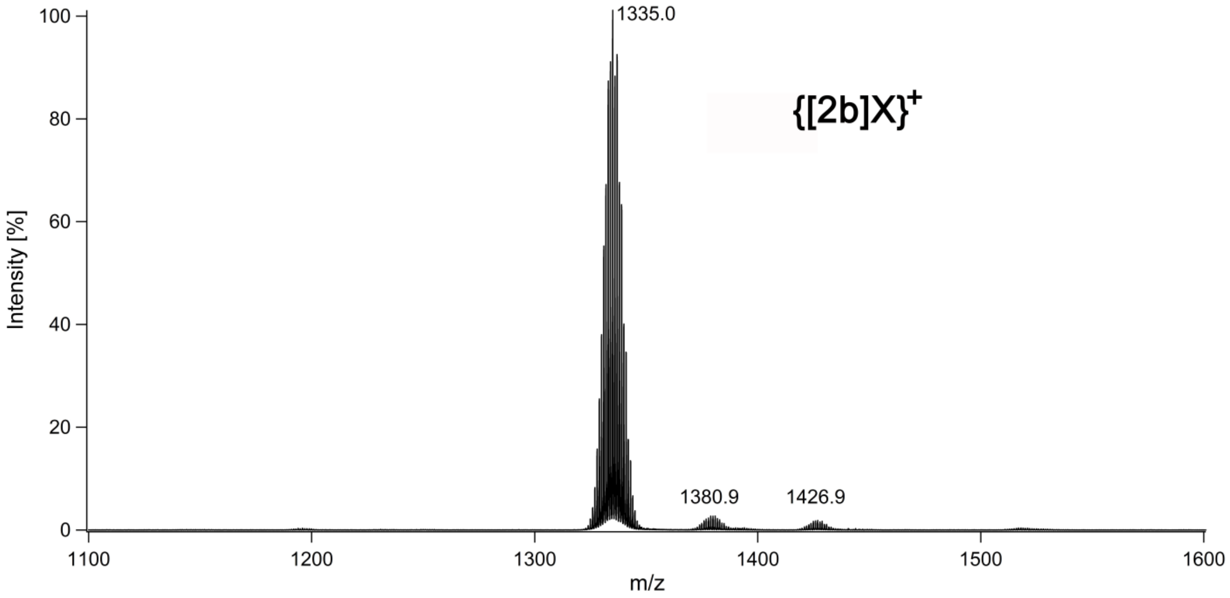

Fig. S8. Mass spectrum obtained by electrospraying [**2b**]X_2 in tetrahydrofuran at an ESI capillary voltage of 4.5 kV. Charge states are indicated as 1+ for different counter ions.

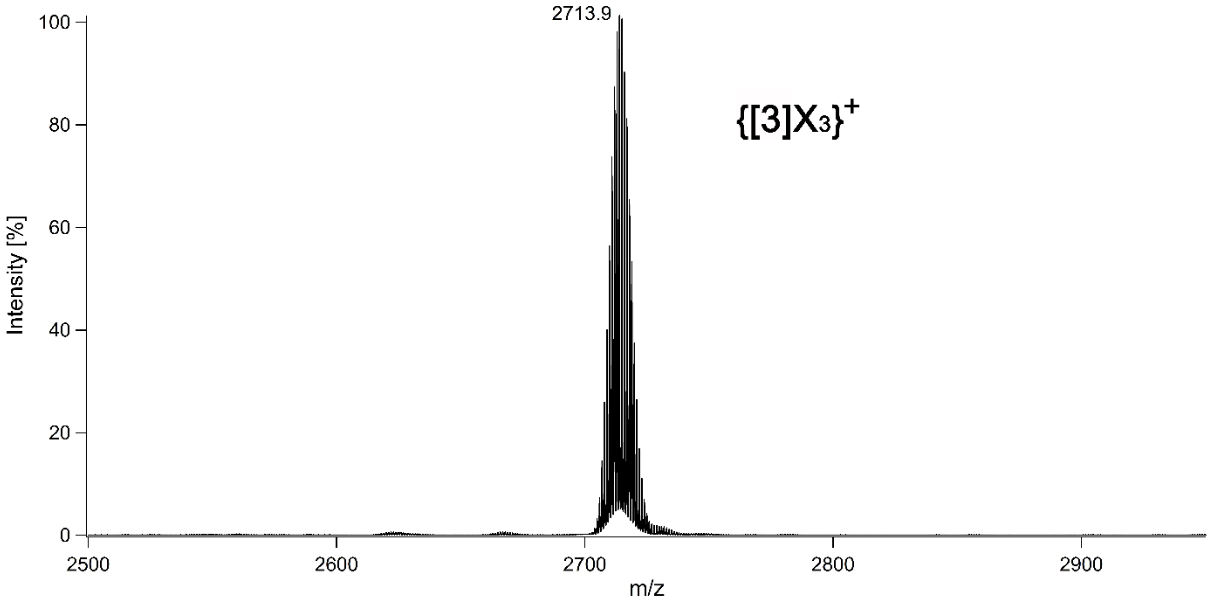

Fig. S9. Mass spectrum obtained by electrospraying [**3**]X_4 suspended in toluene at an ESI capillary voltage of 4.5 kV. Charge states are indicated as 1+ for [**3**]I_3^+.

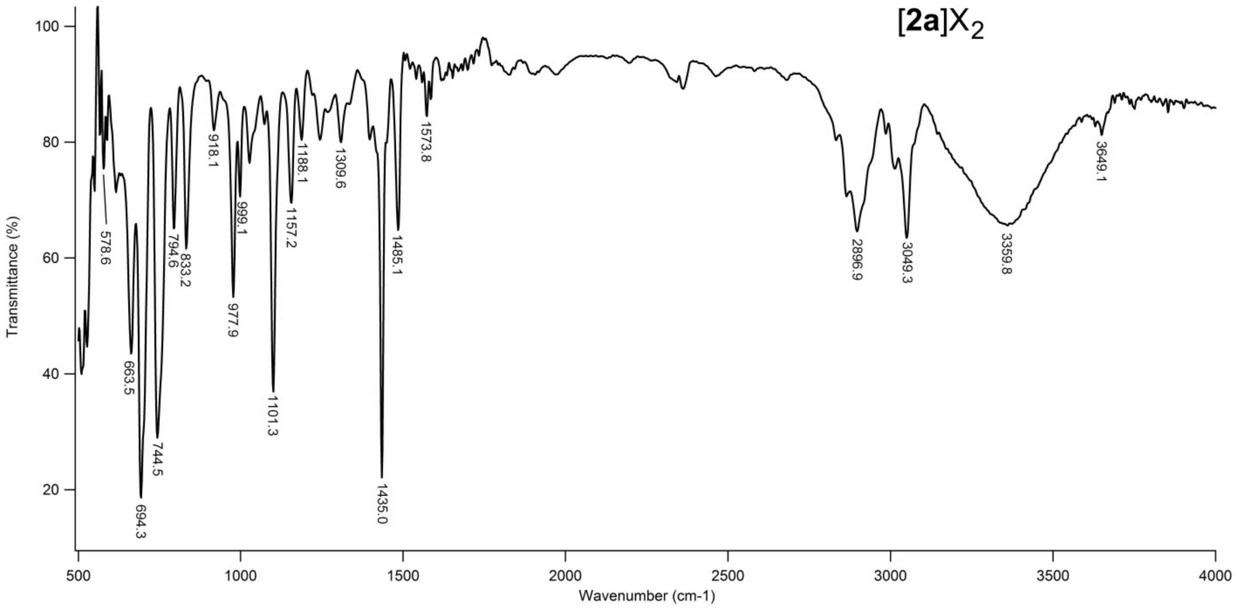

Fig. S10. FT-IR spectrum of [**2a**]X_2 in KBr.

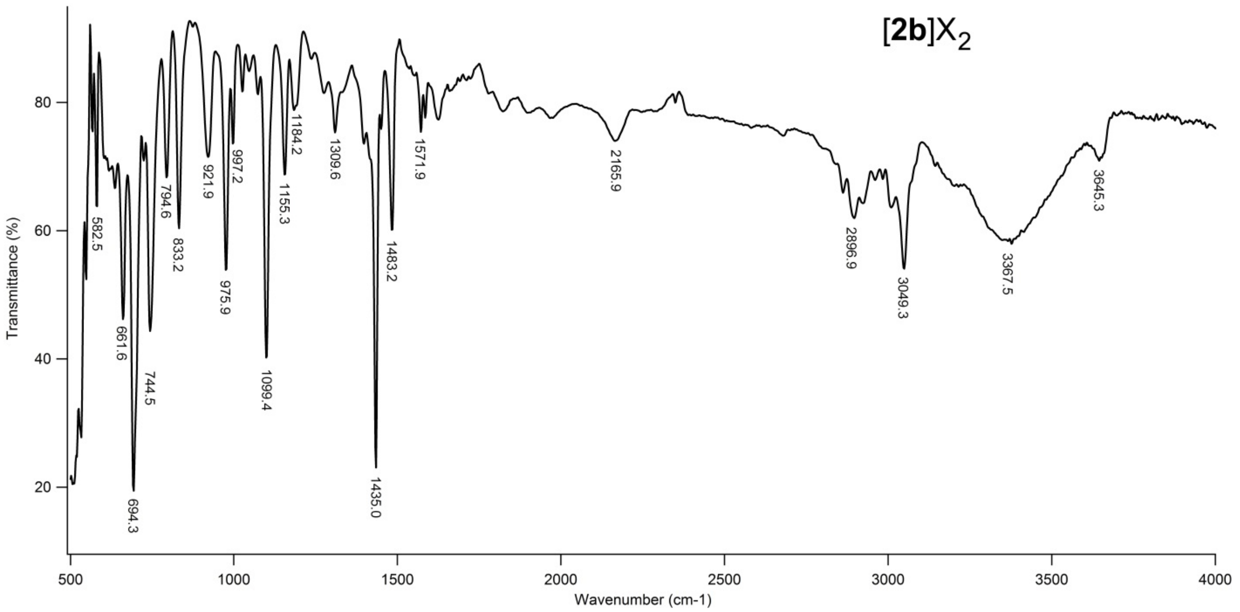

Fig. S11. FT-IR spectrum of [**2b**]X_2 in KBr.

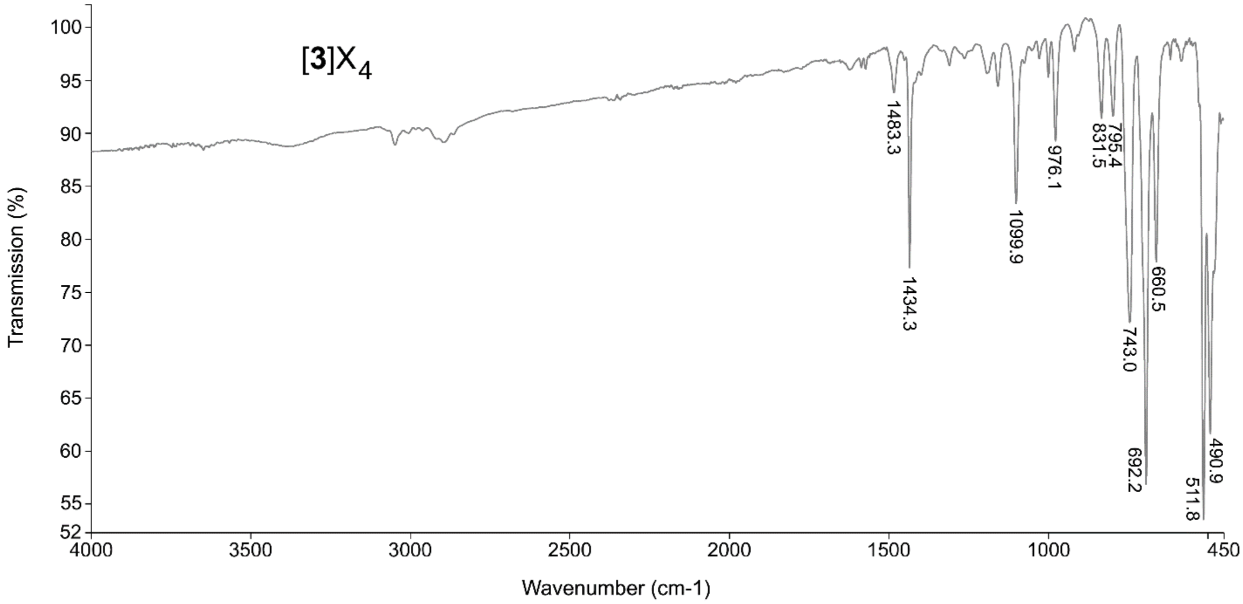

Fig. S12. ATR spectrum of [**3**]X_4.